

# Electrochemical Properties of Thin $\text{Li}_4\text{Mn}_5\text{O}_{12}$ Electrode on $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ Solid Electrolyte

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## Abstract

A fabrication of all-solid-state thin-film rechargeable lithium batteries by a sol-gel method with spin-coating technique is expected to achieve both simplification and cost reduction of fabrication process.  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film electrode is prepared by PVP (polyvinylpyrrolidone) sol-gel method combined with spin-coating on  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$  (LAGP) solid electrolyte. In a cyclic voltammogram, a redox couple is observed at 2.8 vs.  $\text{Li}/\text{Li}^+$  assigned to Li insertion/extraction into/from  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , indicating that the thin film works as an electrode for lithium rechargeable battery. The charge and discharge behaviour have been clearly observed in the charge and discharge test. It is attested that the PVP sol-gel process with the spin-coating technique, which derives both simplification and cost reduction of fabrication process, can be applied to the thin film battery using the LAGP solid electrolyte.

## Keywords

*All-Solid-State Battery; Sol-Gel Method; Thin Film Battery; Lithium Battery; Solid Electrolyte*

## Introduction

All-solid-state thin-film rechargeable lithium ion batteries have received considerable attention as the suitable power sources for some specialized applications, such as smart cards, implantable medical devices, and microelectromechanical systems [Iriyama et. al. (2006), Lee et. al. (2003), Kim et. al. (2003), Jang et. al. (2003), Neudecker et. al. (1999)]. The thin film rechargeable lithium batteries composed of thin-film electrodes and solid electrolytes have been extensively studied on thus far.

In a fabrication process of the thin film batteries, thin films of electrodes, solid electrolyte, and current collectors are sequentially piled-up using various kinds of vapor deposition techniques such as pulsed laser deposition, r.f. magnetron sputtering, and vacuum evaporation [Bates et. al. (2000), Neudecker et.

al. (2000), Lee et. al. (2003), Dudney et. al. (2003), et. Dudney al. (2005), Baba et. al. (2003)]. However, the vapor deposition techniques require high vacuum condition, which leads to complicated and costly fabrication process. For the practical applications of the thin-film batteries, the fabrication process is desirable to be simplified as much as possible. One of the effective methods to overcome above problem will be the use of the sol-gel method combined with spin coating technique. Using the sol-gel and spin coating methods, the fabrication of thin film electrode does not require vacuum condition, leading to the achievement of both simplification and cost reduction of fabrication process.

A fabrication of  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  thin film electrode on  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (LATP) NASICON-type solid electrolyte has been reported by PVP (polyvinylpyrrolidone) sol-gel method and their good electrochemical properties have been achieved[Dokko et. al. (2007), Hoshina et. al. (2005)]. However, electrochemical window of LATP electrolyte is limited by facile reduction of  $\text{Ti}^{4+}$  and this provides restrict application of the LATP [Jiang et. al. (2009), Takada et. al. (2001), Yang, et. al. (2009), Zhang et. al. (2009)] because the narrow window conducts to low energy and power densities of batteries.

$\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$  (LAGP) solid electrolyte is a member of Li ion conductive ceramics with NASION type structure. The total ionic conductivity of LAGP is reported to be  $4.2 \times 10^{-3} \text{ S cm}^{-1}$  [Thokhom et. al. (2010)], which is comparable to LATP. Moreover, the LAGP has an advantage for the electrochemical window because  $\text{Ge}^{4+}$  is insensitive to reduction in contrast with  $\text{Ti}^{4+}$  [Adachi et. al. (1996)]. Therefore, the all-solid-state thin-film rechargeable lithium ion batteries using LAGP electrolyte prepared by the sol-gel method is expected to not only provide high energy and powder

densities, but also achieve both the simplification and cost reduction for fabrication process.

In this paper, the fabrication of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film anode on the LAGP electrolyte by the PVP sol-gel method with the spin-coating and its electrochemical properties have been studied.

## Experimental

LAGP plate ( $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ ) with 300  $\mu\text{m}$  thickness was used in this study [Kotobuki et. al. (2011)].

$\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film electrode was prepared by the PVP sol-gel method with the spin-coating technique. A precursor sol composed of  $\text{CH}_3\text{COOLi}:\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}:\text{i-C}_3\text{H}_7\text{OH}:\text{CH}_3\text{COOH}:\text{H}_2\text{O}:\text{PVP}$  (molecular weight is 55,000) in a molar ratio of 4:5:80:40:200:5 was spin-coated under a rotation speed of 3000 rpm, in order to prepare Li-Mn-O gel film on the LAGP plate. The gel film was converted to  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film by heating at 600°C for 20 min. This process was repeated five times. The weight of prepared  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film was carefully measured by a microbalance.

Morphology of the prepared  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film was observed by a scanning electron microscope (SEM). The characterization of the prepared thin film was carried out by Raman spectroscopy (NRS-1000, Jasco) with 532 nm radiation.

Electrochemical measurements were performed using two electrode configuration. The working electrode was  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  coated on the LAGP solid electrolyte. In order to ensure electrical contact from the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  surface, Au thin film was formed on the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  surface by dc sputtering. Lithium metal was used for counter electrode as well as reference electrode. In order to avoid undesirable reaction between LAGP solid electrolyte and lithium metal, Li ion-loaded poly methyl methacrylate (PMMA) gel-polymer electrolyte was used as a buffer layer. The PMMA gel-polymer electrolyte was prepared by a thermal polymerization. Methyl methacrylate monomer containing ethylene glycol dimethacrylate as crosslinking agent was polymerized in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) containing 1 mol  $\text{dm}^{-3}$   $\text{LiClO}_4$ . Azobisisobutyronitrile (AIBN) was used as a polymerization initiator. The weight ratio of MMA, EGMA, AIBN, and the mixed solvent was 1:0.05:0.02:2.87, respectively. The polymerization was carried out in inert atmosphere at 80°C for 1 h. The thickness of the PMMA gel-polymer was 300  $\mu\text{m}$  and its conductivity was ca.  $1 \times 10^{-3} \text{ S cm}^{-1}$

at room temperature.

Cyclic voltammetry was performed at a scan rate of 10  $\text{mV min}^{-1}$  in a potential range from 2.5 to 3.5 V vs.  $\text{Li/Li}^+$ . A charge/discharge test was also conducted to evaluate an electrochemical performance of the prepared  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film under galvanostatic conditions by using the same cell configuration. Cut off voltages were 2.5 and 3.5 V at charge (lithiation) and discharge (delithiation) processes, respectively. All electrochemical experiments were conducted in an argon-filled glove box at 30°C.

## Results

Figure 1 displays the SEM images of the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film prepared on the LAGP substrate. The surface of the thin film seems rough a little, although no cracks were observed. The thickness of the thin film was estimated to be 0.3  $\mu\text{m}$  from the cross-sectional view. The thin film contacted well with the LAGP substrate and no void between them was observed.

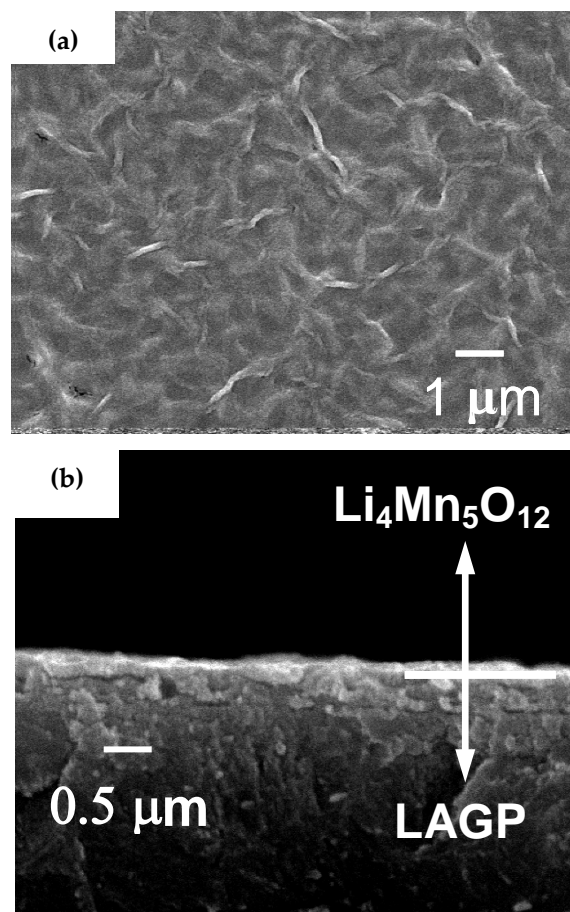


FIG. 1 SEM IMAGES OF (a) SURFACE AND (b) CROSS-SECTION OF  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  THIN FILM ON THE LAGP SUBSTRATE

The Raman spectra of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  fabricated on the LAGP substrate and LAGP itself are revealed in fig. 2. Five Raman bands were detected at 464, 484, 600, 626,

and  $655\text{ cm}^{-1}$  in the spectrum of the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film fabricated on the LAGP. It was obvious that the band at  $464\text{ cm}^{-1}$  was assigned to the LAGP substrate by a comparison with Raman spectrum of LAGP itself. The other bands at  $484$ ,  $600$ , and  $655\text{ cm}^{-1}$  were attributed to  $\text{F}_{1u}$ ,  $\text{F}_{1u}$ , and  $\text{F}_{2u}$  bands of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , respectively [Julien et. al. (2004)]. The vibrational mode of the band at  $626\text{ cm}^{-1}$  was not assigned yet, but it has been thought that the band was due to Mn-O stretching modes. Other phases were not detected in the Raman spectrum of the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film.

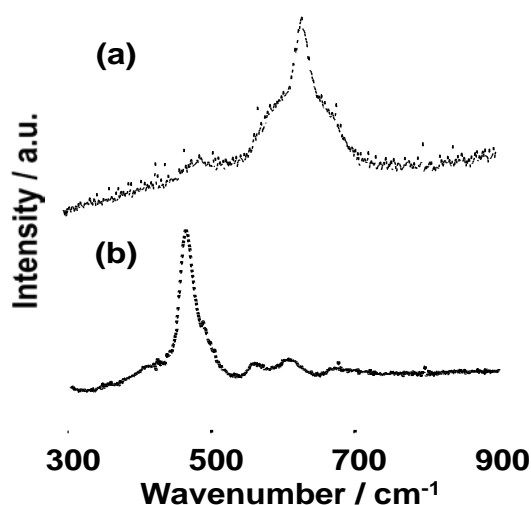


FIG. 2 RAMAN SPECTRA OF (a)  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  THIN FILM ON THE LAGP SUBSTRATE AND (b) LAGP SUBSTRATE

Figure 3 shows a cyclic voltammogram of the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film prepared on the LAGP solid electrolyte. An anodic peak was observed around  $3.1\text{ V vs. Li/Li}^+$  and a cathodic peak was confirmed at  $2.8\text{ V}$ . These peaks corresponded to Li insertion/extraction into/from  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  [Kim et. al. (1998)]. This reversible electrochemical behavior implied that the Li ion transfer between  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  and LAGP took place reversibly.

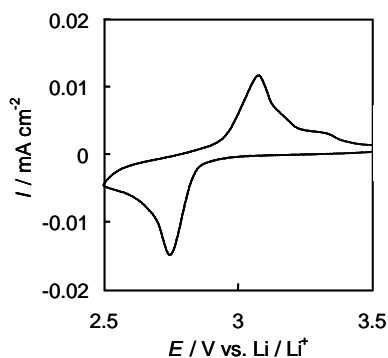


FIG. 3 CYCLICVOLTAMMOGRAM OF  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  THIN FILM ON THE LAGP AT A SCAN RATE OF  $10\text{ mV MIN}^{-1}$

Charge and discharge curves of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film on

LAGP substrate have been revealed in fig. 4. A potential plateau around  $2.8\text{ V}$  in the charge and discharge curves was ascribed to intrinsic redox potential of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  [Kim et. al. (1998)]. In the first cycle, the charge and discharge capacities were  $36$  and  $25\text{ mA h g}^{-1}$ , respectively. Observed irreversible capacity corresponded to irreversible electrochemical reaction. The irreversible capacity was also confirmed in the second cycle. The discharge capacity in the second cycle was  $22\text{ mA h g}^{-1}$ , which was  $14\%$  of theoretical capacity of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  ( $163\text{ mA h g}^{-1}$ ) [Kim et. al. (1998)].

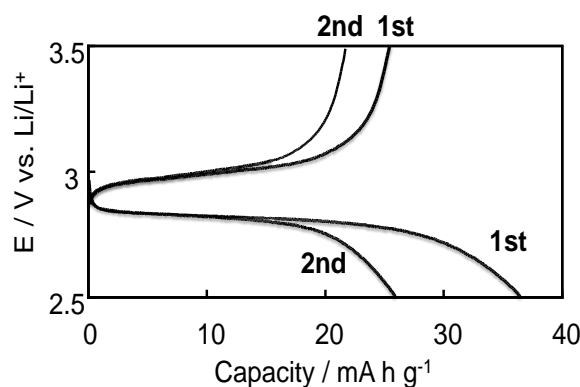


FIG. 4 CHARGE AND DISCHARGE CURVES OF Li/PMMA-gel/LAGP/ $\text{Li}_4\text{Mn}_5\text{O}_{12}$  CELL MEASURED AT  $0.1\text{C}$  ( $4.5\text{ mA cm}^{-2}$ ) RATE

## Discussion

In this study, thin  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  film on the LAGP substrate was prepared by the sol-gel method combined with spin-coating and its electrochemical properties were evaluated.

The Raman spectrum of prepared thin film revealed characteristic Raman bands attributed to  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ . These peaks indicated that the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  could be prepared through our sol-gel procedure.

The  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film demonstrated clear a redox couple in the cyclic voltammogram. The redox couple was appeared around at  $3.1$  and  $2.8\text{ V vs. Li/Li}^+$  in the anodic and cathodic scans, respectively. The redox couple corresponded to the characteristic redox couple of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  [Kim et. al. (1998)], implying that the prepared  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  thin film was able to do Li insertion and extraction reversibly.

In the charge and discharge test, clear potential plateau was observed at  $2.8\text{ V}$ , indicating that the prepared thin film was electrochemically active and worked as electrode for rechargeable lithium battery. However, the discharge capacity, which means the capacity when Li was extracted from the  $\text{Li}_4\text{Mn}_5\text{O}_{12}$

thin film was small, 22 mA h g<sup>-1</sup> in the second cycle which was only 14% of the theoretical capacity. The irreversible capacity was also observed. The most possible reason of the irreversible and small capacity would be due to impurity phases formed at interface between electrode and electrolyte. The impurity phases would be formed during calcination at interface between Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> and LAGP substrate and would act as a resistance layer. Therefore, inferior capacity was observed. To check this hypothesis, TEM-EDX measurement at interface between Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> and LAGP is performed at moment.

In order to improve the capacity, a preparation of buffer layer between electrode and electrolyte is very useful. Hoshina et. al. reported that the capacity of thin LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> electrode on the LATP electrolyte was improved by TiO<sub>2</sub> buffer layer sitting between electrode and electrolyte [Hoshina et. al. (2012)].

The Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> thin film electrode was successfully prepared on the LAGP electrolyte by the sol-gel process with the spin-coating and worked as the negative electrode for lithium rechargeable battery. It is attested that the sol-gel process with the spin-coating, which derives both simplification and cost reduction for fabrication process, can be applied to thin film battery using LAGP solid electrolyte. Further investigation to improve its performance will be made, and new findings will be reported.

## Conclusion

The Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> thin film electrode was prepared by the PVP sol-gel method combined with spin-coating on the LAGP solid electrolyte which has wide electrochemical window. The thin film contacted well with LAGP substrate and no void between the substrate and thin film was observed. The thin film demonstrated clear charge and discharge behaviors and worked as the negative electrode for lithium battery. It is attested that the sol-gel process with the spin-coating, which derives both simplification and cost reduction for fabrication process, can be applied for thin film battery using LAGP solid electrolyte.

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